



Titre: Title:	Constraints on conceptual and quantitative modeling of early diagenetic sediment-hosted stratiform copper mineralization
Auteurs: Authors:	Alexander-C. Brown
Date:	2017
Type:	Article de revue / Journal article
Référence: Citation:	Brown, A.-C. (2017). Constraints on conceptual and quantitative modeling of early diagenetic sediment-hosted stratiform copper mineralization. <i>Minerals</i> , 7(10), p. 1-12. doi:10.3390/min7100192



Document en libre accès dans PolyPublie

Open Access document in PolyPublie

URL de PolyPublie: PolyPublie URL:	https://publications.polymtl.ca/3586/
Version:	Version officielle de l'éditeur / Published version Révisé par les pairs / Refereed
Conditions d'utilisation: Terms of Use:	CC BY



Document publié chez l'éditeur officiel

Document issued by the official publisher

Titre de la revue: Journal Title:	Minerals
Maison d'édition: Publisher:	MDPI
URL officiel: Official URL:	https://doi.org/10.3390/min7100192
Mention légale: Legal notice:	

**Ce fichier a été téléchargé à partir de PolyPublie,
le dépôt institutionnel de Polytechnique Montréal**

This file has been downloaded from PolyPublie, the
institutional repository of Polytechnique Montréal

<http://publications.polymtl.ca>

Article

Constraints on Conceptual and Quantitative Modeling of Early Diagenetic Sediment-Hosted Stratiform Copper Mineralization

Alex C. Brown [†]

École Polytechnique de Montréal, Montreal, QC H3C 3A7, Canada; acbrown@polymtl.ca

[†] Current address: 13250 rue Acadie, Pierrefonds, QC H9A 1K9, Canada.

Received: 8 August 2017; Accepted: 5 October 2017; Published: 13 October 2017

Abstract: Early diagenetic sediment-hosted stratiform copper (eSSC) mineralization results from low-temperature cuprous chloride complexes carried by saline aqueous solution circulating through footwall aquifers. Favorable copper solubilities are attained in moderately oxidizing, near-neutral pH solutions. That specific oxidation level is not determined by co-existence with hematite, with its near-indiscriminant control over Eh. Instead, redbed footwall aquifers are signatures of diagenetic oxidation. Relentless in-situ oxidation of ferrous minerals in redbeds produces pore waters too reduced to transport copper, thus eliminating compaction waters as ore solutions. Continuous early influxes of descending oxygen-rich meteoric waters which have assimilated evaporitic salts may redden aquifers and still retain oxidation levels capable of carrying copper to form downstream eSSCs.

Keywords: early diagenetic sediment-hosted stratiform copper (eSSC); genetic modeling; compaction-driven; topography-driven; meteoric water; oxidation (Eh)-pH controls

1. Introduction

Most of our efforts to design genetic models for sediment-hosted stratiform copper (SSC) deposits are reasonable and well-conceived. Nevertheless, input variables may be difficult to quantify and structure (e.g., when did mineralization occur relative to other events?), and quantitative modeling is often difficult or beyond our reach. Our science is highly descriptive and our analyses may be open to various interpretations. On the other hand, some observations require near-inescapable interpretations, which in turn constrain and strengthen our interpretations. The intent of this communication is to urge close attention to chemical constraints on certain parameters (e.g., oxidation levels of ore solutions) used in designing models for the early diagenetic stage of sediment-hosted stratiform copper (eSSC) mineralization.

2. Background

Early attempts to model the early diagenetic stage of sediment-hosted stratiform copper (eSSC) mineralization began at the deposit-scale. Replacement textures and sulfide zonings indicated that low-temperature cupriferous brines infiltrated fine-grained basal graybeds from coarse-grained footwall redbeds. Disseminated copper sulfides were deposited by replacement of disseminated syndiagenetic pyrite [1–5]. Early semi-quantitative modeling followed, both at the deposit-scale [6,7] and basin-scale [8].

All modeling considered here presumes that copper was deposited during early diagenesis, at low temperatures, and soon after deposition of the host graybeds in intracontinental rift settings (Figure 1). All eSSCs are younger than 2.4 Ga (i.e., post-Great Oxidation Event [9,10]) in age, strongly suggesting that their formation required an interplay with atmospheric oxygen. Further, all eSSCs are associated with intracontinental rifts occurring at low-paleolatitudes, under hot, dry climates, and are almost

invariably associated with evaporites and immature, fine- to coarse-grained footwall redbeds [11–14]. Late stages of sediment-hosted stratiform copper (SSC) mineralization (deposited, for example, during late diagenesis, late veining or orogenic disturbances) are not discussed here.

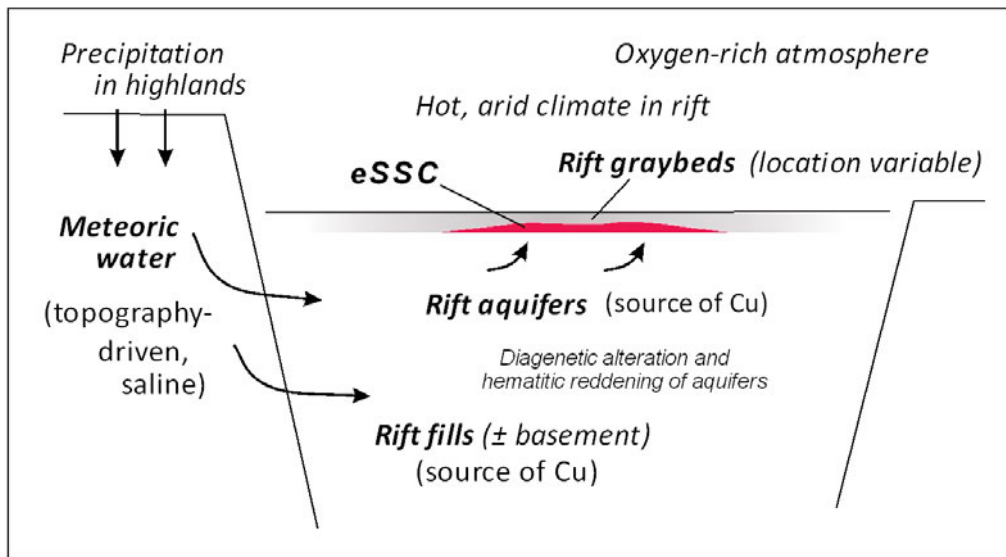


Figure 1. Simplified version of the intracontinental rift setting in which early diagenetic sediment-hosted stratiform copper (eSSC) deposits may form, with portrayal of the basic topography-driven (highland recharge-driven) meteoric water model favored in this communication.

Figure 2, from the 1960s, showed that copper was significantly soluble as chloride complexes (>6 ppm) in low-temperature brines and in the presence of hematite, the prominent pigment of redbeds which commonly underlie eSSCs [6,7]. Although only recognized much later to be misleading, the implication was that the ferric oxide of the redbeds signaled oxidizing conditions and therefore the hematite of footwall redbeds assured that conditions were suitably oxidizing for transporting copper. At the time, our understanding of the solubility of copper seemed chemically complete and sufficient for designing basin-scale models (e.g., [8,15–20]).

Two prominent general models emerged to explain the transport of eSSC-stage copper at the basin scale: (a) compaction-driven cupriferous pore (connate) waters [8,17,18]; and (b) topography-driven (i.e., highland recharge-driven) cupriferous meteoric water (e.g., [8,21]). Both models were found to be plausible according to White [8] in his classic paleohydrologic modeling of the White Pine deposit, northern Michigan, assuming that the brine carried 50 ppm copper (considered reasonable, given that Figure 2 shows that concentrations of 6 to 64 ppm copper are feasible and that lower copper concentrations would require unreasonably large volumes of ore solution to form an ore deposit).

Swenson et al. [18] presented a more rigorous computer-driven compaction model for the White Pine eSSC-type mineralization (see below). They declined to present a highland recharge-driven model, stating that “the timing of main-stage ore deposition occurred during active rifting and prior to compressional tectonism in the region.” [18] (p. 5). The 200 m-thick Nonesuch graybeds and their basal eSSC-type mineralization are enclosed between a 2 km-thick footwall Copper Harbor Conglomerate and a 4 km-thick hanging wall Freda Sandstone, both presumed to have been basin-wide post-rift erosional products of concurrent rift highlands [22], which should have induced topography-driven flow within the adjacent rift basin aquifers, including the footwall Copper Harbor Conglomerate.

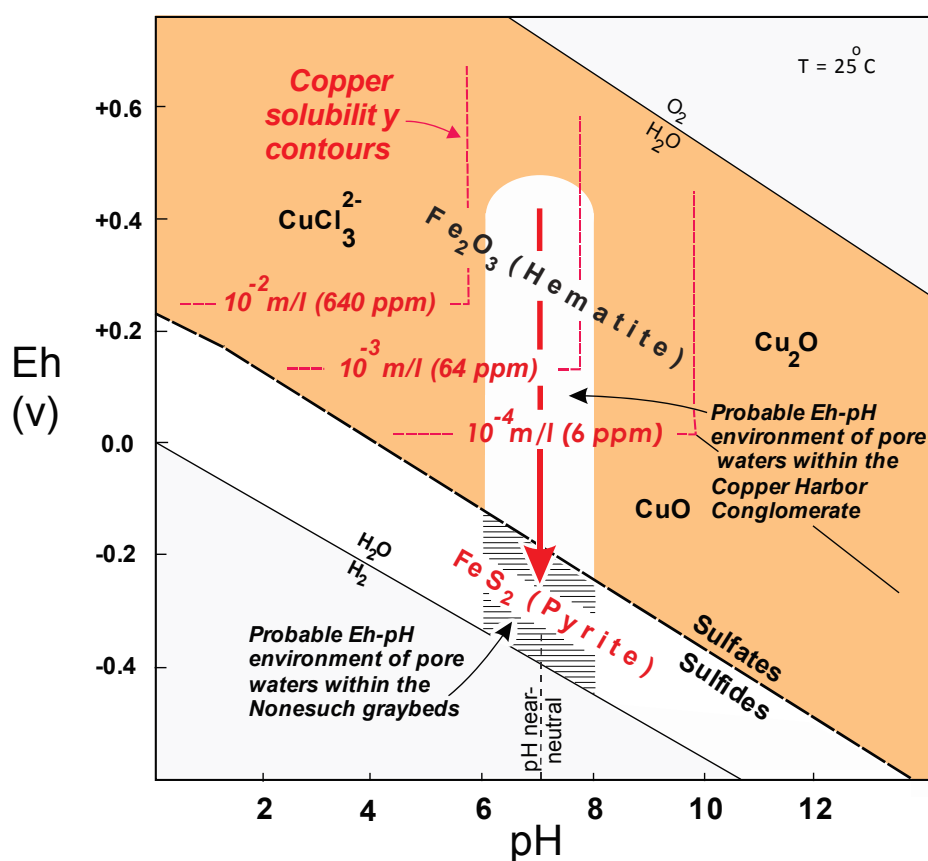


Figure 2. Initial Eh-pH stability diagram showing conditions suitable for high copper solubilities as cuprous chloride complexes in a low-temperature brine (see white area extending across the stability fields of hematite (orange) and sulfates), as applied to the redbed/graybed setting of the White Pine eSSC deposit, northern Michigan. Copper, transported as chloride complexes through the footwall Copper Harbor Conglomerate aquifer, is deposited as sulfides upon entering the pyritic Nonesuch graybeds (see the chemical path indicated by the descending red arrow). Modified after Brown [6,7].

3. Relating Copper-Favorable Eh-pH Conditions to Natural Environments

Eh-pH conditions suitable for copper transport, as defined in Figure 2, may be related to natural low-temperature aqueous environments identified earlier by Garrels [23] (see also Garrels and Christ [24]). Consider typical Eh-pH conditions measured in the field for (a) rain and surface waters (i.e., oxygen-rich and slightly acidic, due to equilibration with atmospheric oxygen and carbon dioxide: see the upper gray ellipse of Figure 3); and for (b) deep groundwater isolated from the Earth's atmosphere (i.e., oxygen-poor due to the oxidation of ferrous minerals, and essentially pH-neutral due to reactions with subsurface carbonates and/or the acid-consuming hydrolysis of labile silicate minerals: see the lower gray ellipse of Figure 3). These two types of natural water may be equated, respectively, with (a) surface water draining into subsurface environments to become meteoric water (upper gray ellipse), and (b) meteoric water descending slowly into the subsurface, such as into rift-marginal highlands and then along aquifers within rift-basin fills, to become deep, oxygen-depleted groundwater (lower gray ellipse). The descending red arrow traces the evolution of near-surface meteoric water into deep oxygen-depleted meteoric water. By overprinting these natural environments with a basic stability diagram for Fe-O-H₂O, it is clear that the evolution of oxygen-rich near-surface meteoric water into reduced deep groundwater (red arrow) is brought about by Eh-buffering (oxygen-consuming) reactions with ferrous minerals (see proxy magnetite in Figure 3).

having stability fields below the lower gray ellipse. Note also that once the Eh-pH conditions depicted by the lower gray ellipse have been attained, Eh conditions cannot change significantly thereafter because of the persistent buffering by ferrous minerals and the continuous isolation of deep water from atmospheric oxygen.

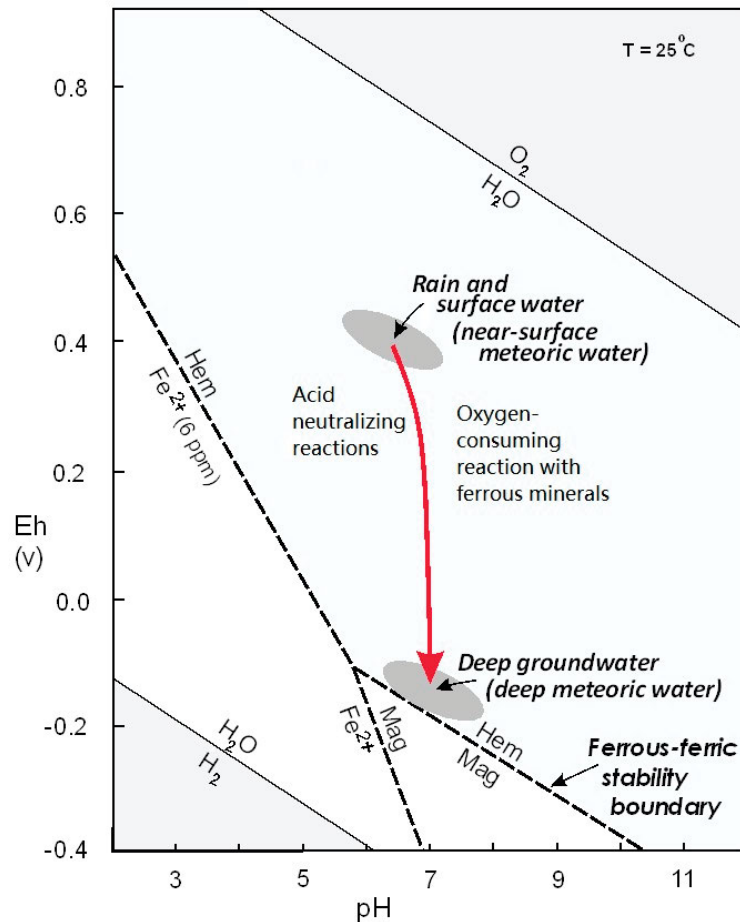


Figure 3. Low-temperature Eh-pH stability diagram showing two crucial environments taken from Garrels [23,24]: those of rain and surface water which may be taken to represent early meteoric water descending into rift-marginal highlands (oxygen-rich and slightly acidic; upper gray ellipse); and of deep groundwater which represents deep meteoric water (pH neutral and oxygen-depleted; lower gray ellipse). The descending red arrow suggests the evolution of the Eh-pH characteristics of the near-surface meteoric water as: (a) its acidity is neutralized by carbonates and/or acid-consuming hydrolysis of silicate minerals; and (b) its oxygen is consumed by chemical buffering with the ferrous mineral content of its aquifers, to produce authigenic hematite and thus diagenetically redden its aquifers. The lower gray ellipse lies close to the magnetite-hematite stability boundary (a proxy ferrous-ferric boundary) due to near-complete depletion of oxygen in the pore water. See text for further explanations. Modified after Brown [21].

Meanwhile, Rose [25,26] had constructed a more rigorous Eh-pH stability diagram for copper solubilities showing, more precisely than in Figure 2, the ideal Eh-pH conditions for high copper solubilities (Figure 4). Conditions for copper solubility at 100 °C are similar to those at 25 °C [26]. Under near-neutral pHs and moderately oxidizing Eh levels (+0.25 to 0.0 V), copper solubilities may be 64 ppm or even higher (see the central gray ellipse of Figure 4). Elsewhere in the diagram, copper solubilities are insignificant (both above and below the +0.25 to 0.0 volt range, and at unrealistically

low or high pHs). Note that those particular Eh-pH conditions suitable for high copper solubilities lie directly along the downward-evolving trend between near-surface meteoric water (uppermost gray ellipse, from Figure 3) and deep meteoric water essential deprived of oxygen (lowermost gray ellipse) (see [21]). If the descending early meteoric water were to leach subsurface evaporites and/or mix with dense brines actively descending from evaporite pans at surface, this mobile pore solution would become a moderately oxidized, low-temperature brine ideally suited to transport copper as it enters the central gray ellipse (see the head of the descending red arrow of Figure 4). Evaporites have long been recognized as closely affiliated with eSSCs [11,15], as might be expected considering the close association of eSSCs with hot, arid global environments within intracontinental rifts occurring at low paleolatitudes [14,15]. Then the brine only needs to be provided with a source of copper to become a cupriferous ore solution [21,27].

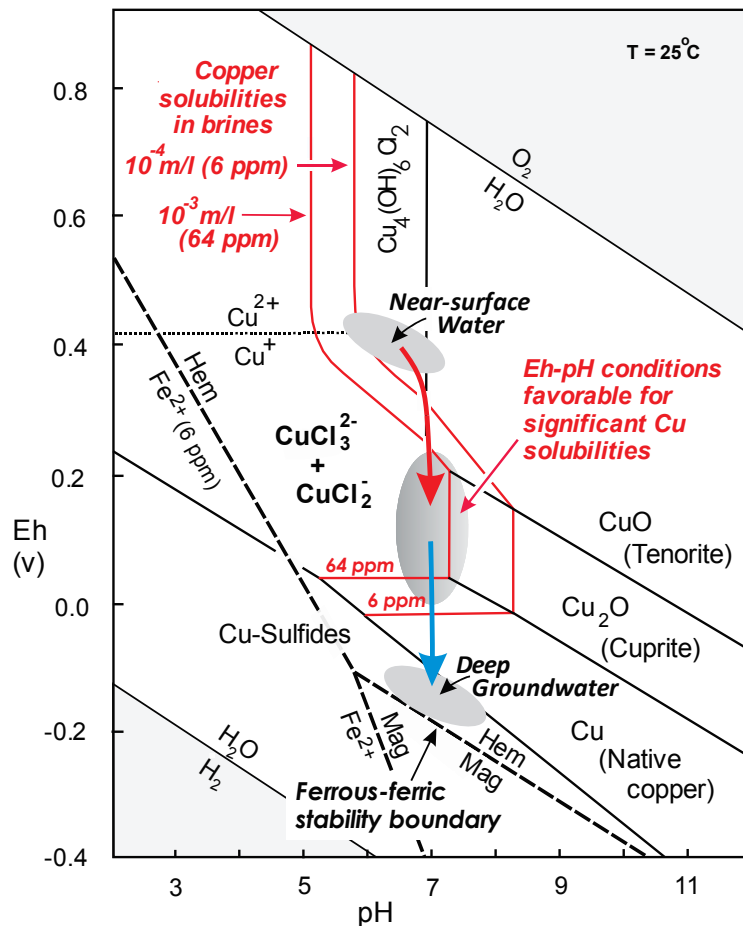


Figure 4. Solubility of copper as cuprous chloride complexes in a low-temperature brine, modified after Rose [25,26]; and stability fields for basic iron oxides. The diagram is generally applicable up to at least 100 °C [26]. The central gray ellipse outlines Eh-pH conditions most favorable for the solution and transport of copper (Eh = +0.25 to 0.0 V, and near-neutral pH) (from [21]). See Figure 3 for explanations of the uppermost and lowermost gray ellipses. The descending red arrow suggests the evolution of brine originating as meteoric water and descending continuously through aquifers containing labile ferrous minerals. The descending blue arrow suggests the additional loss of oxygen that compaction water would experience during its long-term in-situ chemical buffering by labile ferrous minerals, before its expulsion and mobilization by compaction. See text for further explanations.

4. Sources of Copper

The copper found in early diagenetic SSC-type mineralization is generally thought to have originated from non-igneous, non-orogenic sources, and is widely thought to result from leachings of the trace copper content of footwall redbeds and/or associated bimodal volcanics [15,19,20,28]. Where necessary to explain the copper endowment of supergiant SSCs, the leaching of copper may be extended to basement rocks and/or mineralization in basement rocks (e.g., [17,29–31]). Immature porous coarse-grained clastic sediments are particularly attractive both as sources of copper and as aquifers for footwall circulations of cupriferous brines.

The leaching process has been described in detail from petrographic, chemical and SEM studies by Walker [32,33], Zielinski et al. [34] and their colleagues. Their observations on first-cycle clastic sediments (Pliocene, Pleistocene and Modern in age) in the modern Gulf of California rift basin show that these young sediments have already experienced progressive diagenetic alteration of labile mineral constituents over millions of years. The Modern sediments are gray (not yet altered), the Pleistocene are partially reddened, and the Pliocene are fully reddened with diagenetic hematite. The abundance of diagenetic hematite in the older sediments requires that the altered clasts have been well-flushed by oxygen-bearing solutions. The only plausible source of oxygen-rich solutions would be descending meteoric water from the rift-marginal Peninsular Range. This meteoric water could also become saline by the assimilation of evaporitic salts occurring in abundance both in the subsurface and in surface salinas.

Walker and colleagues also determined the trace-level copper contents of labile minerals experiencing diagenetic alteration (see Table 1), and they describe the step-by-step release of this copper to interstitial pore waters [33]. Although the occurrence of downstream graybeds remains unknown, this flow of cupriferous brine could then infiltrate basal graybeds, if encountered, and deposit eSSC-type mineralization. In effect, the Gulf of California is an ideal site for the leaching and transport of copper to form downstream eSSC deposits in modern times. Independent estimates of the time required to form important eSSC deposits tend to call for active circulations of cupriferous brine over millions of years [7,18,27,29].

Table 1. Copper contents of common labile minerals in first-cycle clastic sediments (from Walker [33]).

Minerals	No. of Samples Analyzed	Average Cu Content (ppm)
Pyroxene	90	120
Biotite	660	86
Amphibole	40	78
Magnetite	250	76
Plagioclase	108	62
K-feldspar	70	1–20

5. Chemical Events in Compaction Pore Waters

In-situ chemical changes in pore waters trapped in their sediments until mobilized by the loading and compaction effects of overlying sediments would probably parallel those predicted from the studies of Walker [33] and colleagues. The principal difference may be that the alterations in the water chemistry take place physically within the minute stationary confines of interstitial pore spaces. Nevertheless, chemical bufferings of Eh and pH values by water/mineral exchanges and alterations should follow the near-inescapable path suggested by the red arrow of Figure 3.

Again, the sediment is largely a coarse-grained immature clastic erosional product of rift-marginal highlands, with an abundant ferrous mineral content. The initial oxygen content of the pore water, due to equilibration with atmospheric oxygen at burial, would be consumed relentlessly by oxidation of the ferrous mineral content. Water/mineral equilibration may take place over millions of years of in-situ residence in immature host sediment before mobilization by the loading and compaction effects

of overlying sediments (e.g., approx. 5 million years before expulsion by compaction at White Pine, northern Michigan, according to Swenson et al. [18]).

In-situ alterations in interstitial pores would also release trace-level copper from altered labile minerals. If the pore water were saline, this copper could form a low-temperature cupriferous brine, much as foreseen by Walker [33]. Swenson et al. [18] suggest that the pore water should be saline, given that the pore waters of most sedimentary basins are saline at depth [35]. In fact, in the case of the White Pine eSSC district, evaporitic salts and/or brines were probably contemporaneous with sedimentation in the Keweenaw rift basin due to a prevailing hot, dry climate at $\sim 10^\circ$ N latitude [36], even if evaporites as such are not known within the Keweenaw stratigraphy. As noted by White [37] and others, present-day seeps of water in the deep mine workings are invariably highly saline in the Keweenaw district.

Nevertheless, to transport the released copper during expulsion of compaction water, the oxidation level within the pore water would need to attain and maintain that special mid-level Eh range (+0.25 to 0.0 V) suitable for high copper solubilities. Presumably, progressive consumption of oxygen by ferrous mineral buffering would indeed eventually take the pore solution to that ideal copper solubility range at some point during the pore water's in-situ residence within its host. However, over the millions of years of quiet residence within its host sediment, the depletion in oxygen would normally continue without interruption toward the ferrous-ferric stability boundary (see the red arrow of Figure 3), at which the pore water cannot carry significant amounts of copper. Compaction water is not a promising candidate as an ore solution.

In some modeling, it is simply assumed that the hematite of the host redbed assures that conditions were oxidizing throughout pre-ore time and would therefore favor the dissolution and transport of copper (e.g., [18] (pp. 14–15); [19] (p. 630); [20] (pp. 477–479); [38] (p. 1344). That assumption is highly questionable, on three accounts. First, as indicated above, buffering by ferrous minerals should take the Eh level inevitably to or near the ferrous-ferric stability boundary, at which conditions are distinctly reducing and the solubility of copper is negligible. Second, hematite occupies a vast Eh-pH stability field, basically extending across all Eh-pH environments above the ferrous-ferric stability boundary, and as such, hematite is unable to impose any particular Eh-pH condition within its own stability field, such as the ideal pH-neutral and mid-range Eh suitable for high copper solubilities. Third, as described by Walker [33] and colleagues, the hematitic pigment of rift sediments deposited at low latitudes is largely diagenetic and a co-product of the same subsurface diagenetic alterations which eventually release copper to the pore solutions. In other words, hematite is not a dominant detrital mineral in the original sediment and therefore not available to impose any specific oxidation levels within the sediment's pore solution. In fact, the existence or not of pre-ore detrital hematite in the footwall aquifer is of minor consequence in forming eSSCs because it plays no role in establishing Eh levels necessary for copper solubility and transport. Without further qualification, the pre-ore footwall sediments underlying eSSC deposits may be more aptly identified only as: generally coarse-grained, immature, first-cycle clastic sediments (with or without a detrital hematitic pigment).

6. The White Pine eSSC—A Case in Particular

The SSC mineralization at White Pine, Michigan, has been amongst the most commonly modeled mineralizations of this type, largely because of its early definition by intense drilling and mining in well-preserved host rocks. According to the quantitative computer modeling of the main-stage eSSC-type mineralization by Swenson et al. [18], the mobilization of original connate pore water from the footwall Copper Harbor Conglomerate (the presumed principal source of copper) was by compaction linked to progressive overloading by an approximately 4 km thickness of post-Nonesuch clastics, the Freda Sandstone. The expulsion of compaction water was found to have been strongest during a period ranging from about 5 to 15 million years following deposition of the host Nonesuch graybeds. From the apparent rates of diagenetic alteration, i.e., extending over millions of years [33], it may be presumed that the original pore waters of the Copper Harbor Conglomerate footwall

aquifer had reacted and attained a high level of in-situ water/mineral equilibration during its 5 million-year-long residence within its aquifer before mobilization by compaction. As such, the pore water should have lost most of its original oxygen content, i.e., of that oxygen dissolved at deposition under an oxygen-rich atmosphere (approx. 10 mg/L of water under our present atmosphere, according to Brown [27]), due to in-situ oxidation of the ferrous mineral content of the Copper Harbor Conglomerate [22,39]. The resulting Eh level of the in-situ pore water should then have approached that of the ferrous-ferric stability boundary (i.e., the magnetite-hematite stability boundary): approx. -0.18 V at a near-neutral pH (see the combined descending red and blue arrows of Figure 4). At that Eh level (well below the $+0.25$ to 0.0 V needed for significant copper solubilities), copper could not have been transported at concentrations necessary to form an eSSC deposit from compaction pore water (see the central gray ellipse of Figure 4).

This dilemma was in fact addressed during the quantitative modeling by Swenson et al. [18] (p. 15): “Copper solubility is reduced by approximately four orders of magnitude, if fO_2 is constrained by the Fe_2O_3 - Fe_3O_4 redox buffer.” The authors then proposed that CuO (tenorite, and presumably not cuprite, as stated in their article) could have been the dominant chemical buffer which held the Eh level near that mid-Eh level needed for high copper solubilities (see Figure 4). Tenorite is presumed to have formed by surface oxidation of native copper occurring in unaltered Portage Lake Volcanics flows (a probable source of erosional debris in the Copper Harbor Conglomerate [22,39]). Tenorite, as a dominant Eh buffer, would need to have prevailed over the ferrous mineral content of the Copper Harbor Conglomerate, and yet tenorite is not listed as a common heavy-mineral constituent of the Copper Harbor (see, for example, [22]). Furthermore, it is questionable whether, at that time, adequate amounts of native copper occurred within the Portage Lake Volcanics to have generated significant amounts of tenorite by surficial oxidation (note in passing: the famous native copper ores of the Keweenaw district are hosted by the Portage Lake Volcanics, but postdate the main-stage eSSC-type copper at White Pine). Further, Walker [40] and colleagues note that surface oxidation tends to be minor under the hot, arid climates prevailing in low-latitude rift environments; would the oxidation of any available native copper not have been minimal under such climatic conditions?

The compaction models of White [8] and Swenson et al. [18] rely on the Porcupine Volcanics dome as a partial barrier to cupriferous solutions driven southward out of the Keweenaw rift basin along the footwall Copper Harbor aquifer. The solutions would have been constricted and forced upward by thinning of the aquifer to about 150 m over the buried dome. However, as explained elsewhere [41], most of the southward-driven flow through the Copper Harbor aquifer should have escaped laterally around the Porcupine Volcanics dome barrier, to the east and west of the apparent footwall barrier, where the ~100 km-wide volcanic dome (E–W dimension) pinches out and the Copper Harbor maintains its normal ~2 km thickness. In fact, Swenson et al. [18] tested the possibility that Copper Harbor flow might not be driven upward into the base of the overlying Nonesuch graybeds where the Porcupine Volcanics dome is absent. They found that most of the flow would have continued southward unimpeded within the 2 km-thick Copper Harbor aquifer and would not have significantly infiltrated the basal Nonesuch aquitard to form eSSC-type mineralization. Seen thus, the compaction model does not appear to be hydrogeologically viable for White Pine.

7. Other eSSCs

The perspectives developed here may have applications elsewhere. Basin-scale modelings of various types have been applied to the well-preserved and intensely studied Kupferschiefer mineralization, for example (e.g., [16,17,20]). Jowett’s [16] early, thermally driven model depended on an exceptionally copper-rich pore solution, deep rift-basin temperatures above 200 °C and a late-diagenetic timing. Cathles et al. [17] also presumed a late-diagenetic timing and called upon deep compaction to drive oxidized cupriferous fluids. Borg’s [20] “work-in-progress” model attributes the main pulse of multi-stage mineralization to oxidized fluids driven up from Rotliegende redbeds and associated volcanics, in addition to warm fluids released by fractured basement rocks, about 105

million years after Kupferschiefer sedimentation [42]. In each case, the timings of mineralization are distinctly not early diagenetic, and could be excluded from further comment here. However, each also relies on the footwall Rotliegende redbeds to provide oxidizing conditions suitable for copper transport, whereas it is evident from the abundance of associated ferrous minerals in footwall units that the ore solutions should have equilibrated to reduced Eh levels, too reduced for the transport of copper. The Kupferschiefer seems not yet to have been modeled using descending oxygen-rich meteoric water.

Although numerous other SSC deposits seem to have early diagenetic copper (e.g., far western segments of the Central African Copperbelt and perhaps the argillite-hosted portions of the Zambian deposits; Creta, Oklahoma; Redstone, NW Territories, Canada; Salta, NW Argentina), modeling has generally been conceptual, with minor details aside from the acknowledgment that ore solutions must be oxidizing. The restricted Eh-pH conditions for copper transport favors a topography-driven meteoric model to provide a large input of water that attains moderate oxidation levels.

In some cases (e.g., some Zambian deposits [43] and the Redstone mineralization [44]), the traditional early diagenetic copper sulfides disseminated along bedding are accompanied by similar sulfides in bedding-parallel veins and cross-cutting veins. It may be argued that the vein mineralization was remobilized from the previously mineralized wallrocks (employing the early diagenetic model, then post-ore deformation and remobilization, for example). Or that the disseminated sulfides in wallrocks and in veins resulted from a single circulation of ore solutions, after or coincident with late structural deformation. Arguments developed in this paper would seem to favor the first interpretation, if the transport of copper is dependent on a specific moderately oxidizing Eh level. Late fluids rising from deep basin levels would have been isolated from atmospheric oxygen fluids for long periods and would probably have equilibrated close to the ferrous-ferric stability boundary. Again, long-equilibrated solutions and long isolated from atmospheric oxygen are unlikely to be cupriferous solutions.

In other cases, such as late-stage mineralizations in the Kupferschiefer, similar questions may be raised: if it is acknowledged that the ore solution must be oxidized to transport copper, and it is also recognized that hematite has a basically indiscriminant control over Eh-pH environments within its vast stability field, hematite cannot, on its own, define those particular mid-level Eh-pH conditions needed for high copper solubilities. Thus, a late circulation of brine through hematitic footwall units is probably an insufficient explanation for the occurrence of copper-bearing brines in footwall units. On the other hand, a continuous influx of oxygen-rich meteoric water could attain and maintain that ideal Eh-pH environment for copper transport.

8. Conclusions

Deposit-scale modelings of early diagenetic sediment-hosted stratiform copper deposits are generally well-founded, following multiple studies of well-preserved examples (e.g., the Kupferschiefer, White Pine, western Copperbelt deposits, Creta, Redstone, Salta). Modelings at the basin scale have generally been conceptual, with limited success in quantifying ore-forming systems. The principal point of this communication is that chemical environments, notably Eh-pH levels, place certain seemingly inescapable constraints on the genesis of suitable cupriferous ore-forming solutions. Progressive chemical bufferings with labile silicates and/or carbonates should assure that pHs converge toward near-neutral levels, whether mobilized by compaction or topography. However, it appears that a clear distinction may be made between the plausibilities of the two most prominent basin-scale models for early diagenetic SSCs, based on their characteristic Eh buffering paths: compaction-driven circulations of oxygen-deficient footwall brines (e.g., [17,18,20]), vs. topography-driven flows of initially oxygen-rich meteoric water [21]. By in-situ chemical equilibration with the ferrous mineral content of its host, compaction water probably becomes too reduced to carry significant amounts of copper. And once too-reduced, there are no means to regain moderately oxidized Eh levels. The hematite of redbeds, the most commonly invoked

deep source of oxygen, is in fact unable chemically to direct Eh levels to those mid-Eh levels necessary to carry copper.

On the other hand, descending meteoric water, previously equilibrated with atmospheric oxygen, may continuously attain ideal Eh-pH levels for copper transport by the same progressive equilibration with the labile mineral content of its aquifers. Long-term influxes of large volumes of meteoric water with mid-range Eh levels are then necessary to dissolve and transport copper to downstream graybeds and to deposit this copper as early diagenetic SSC-type mineralization.

Acknowledgments: This article is dedicated to the memory of Theodore ‘Redbed Ted’ Walker, recently deceased after a long and distinguished career at the University of Colorado-Boulder. His life-long research was given enthusiastically to the study and understanding of hematitic redbeds and sharing his knowledge with others. The author sincerely appreciates the numerous improvements suggested by the two reviewers and guest editor.

Conflicts of Interest: The author declares no conflict of interest.

References

1. White, W.S. The White Pine copper deposit. *Econ. Geol.* **1960**, *55*, 402–410. [[CrossRef](#)]
2. Bartholomé, P. *Les Minerais Cupro-Cobaltifères de Kamoto (Katanga-Ouest). Pt. I. Pétrographie, Pt. II. Paragenèse*; Studia Universitatis Louvanum, Faculté des Sciences: Leopoldville, Kinshasa, 1962; Volume 14, pp. 3–40.
3. Brown, A.C. Mineralogy at the Top of the Cupriferous Zone, White Pine Mine, Ontonagon County, Michigan. Master’s Thesis, University of Michigan, Ann Arbor, MI, USA, 1965; p. 81.
4. Brown, A.C.; Trammell, J.W. Zoning of the White Pine Copper Deposit, Ontonagon County, Michigan. *Econ. Geol.* **1965**, *60*, 1308. [[CrossRef](#)]
5. White, W.S.; Wright, J.C. Sulfide-mineral zoning in the basal Nonesuch Shale, northern Michigan. *Econ. Geol.* **1966**, *61*, 1171–1190. [[CrossRef](#)]
6. Brown, A.C. Zoning in the White Pine Copper Deposit, Ontonagon County, Michigan. Ph.D. Thesis, University of Michigan, Ann Arbor, MI, USA, 1968; p. 199.
7. Brown, A.C. Zoning in the White Pine Copper Deposit, Ontonagon County, MI, USA. *Econ. Geol.* **1971**, *66*, 543–573. [[CrossRef](#)]
8. White, W.S. A paleohydrologic model for mineralization of the White Pine copper deposit, northern Michigan. *Econ. Geol.* **1971**, *66*, 1–13. [[CrossRef](#)]
9. Cloud, P. Atmospheric and hydrospheric evolution on the primitive Earth. *Science* **1968**, *160*, 729–736. [[CrossRef](#)] [[PubMed](#)]
10. Holland, H.D. Sedimentary mineral deposits and the evolution of Earth’s near-surface environments. *Econ. Geol.* **2005**, *100*, 1489–1509. [[CrossRef](#)]
11. Davidson, C.F. A possible mode of origin of strata-bound copper ores. *Econ. Geol.* **1965**, *60*, 942–954. [[CrossRef](#)]
12. Kirkham, R.V. Sediment-hosted stratiform copper. In *Geology of Canadian Mineral Deposit Types*; Eckstrand, O.R., Sinclair, W.D., Thorpe, R.L., Eds.; Geology of Canada Series No. 8 (also Geological Society of America, Geology of North America Series P-1); Geological Survey of Canada: Ottawa, ON, Canada, 1995; pp. 223–233.
13. Brown, A.C. Global constraints on the genesis of stratiform copper deposits. In *Centenaire des Premières Études sur la Géologie Shabienne (Zaire): International Cornet Symposium*, 1994; Charlet, J.-M., Ed.; Gisements Stratiformes de Cuivre et Minéralisations Associées: Mons, Belgium, 1996; pp. 93–102.
14. Brown, A.C. World-class sediment-hosted stratiform copper deposits: Characteristics, genetic concepts and metallotects. *Aust. J. Earth Sci.* **1997**, *44*, 317–328. [[CrossRef](#)]
15. Kirkham, R.V. Distribution, setting and genesis of sediment-hosted stratiform copper deposits. In *Sediment-Hosted Stratiform Copper Deposits*; Boyle, R.W., Brown, A.C., Jefferson, C.W., Jowett, E.C., Kirkham, R.V., Eds.; Special Paper 36; Geological Association of Canada: St-John’s, NL, Canada, 1989; pp. 3–38.
16. Jowett, E.C. Genesis of Kupferschiefer Cu-Ag deposits by convective flow of Rotliegende brines during Triassic rifting. *Econ. Geol.* **1986**, *83*, 1823–1837. [[CrossRef](#)]

17. Cathles, L.M., III; Oszczepalski, S.; Jowett, E.C. Mass balance evaluation of the late diagenetic hypothesis for Kupferschiefer Cu mineralization in the Lubin basin of southwestern Poland. *Econ. Geol.* **1993**, *88*, 948–956. [[CrossRef](#)]
18. Swenson, J.B.; Person, M.; Raffensperger, J.P.; Cannon, W.F.; Woodruff, L.G.; Berndt, M.E. A hydrogeological model of stratiform copper mineralization in the Midcontinent Rift System, northern Michigan, USA. *Geofluids* **2004**, *4*, 1–22. [[CrossRef](#)]
19. Hitzman, M.W.; Selley, D.; Bull, S. Formation of sedimentary rock-hosted stratiform copper deposits through Earth history. *Econ. Geol.* **2010**, *105*, 627–639. [[CrossRef](#)]
20. Borg, G.; Piestrzynski, A.; Bachmann, G.H.; Puttmann, W.; Walther, S.; Fieldler, M. An overview of the European Kupferschiefer deposits. In *Geology and Genesis of Major Copper Deposits and Districts of the World—A Tribute to Richard H. Sillitoe*; Special Publication No. 16; Hedenquist, J.W., Harris, M., Camus, F., Eds.; Society of Economic Geologists: Littleton, CO, USA, 2012; pp. 455–486.
21. Brown, A.C. Refinements for footwall red-bed diagenesis in the sediment-hosted stratiform copper deposits model. *Econ. Geol.* **2005**, *100*, 765–771. [[CrossRef](#)]
22. Daniels, P.A., Jr. Upper Precambrian sedimentary rocks: Oronto Group, Michigan-Wisconsin. *Geol. Soc. Am. Mem.* **1982**, *156*, 107–133.
23. Garrels, R.M. *Mineral Equilibria*; Harper and Brothers: New York, NY, USA, 1960.
24. Garrels, R.M.; Christ, C.L. *Solutions, Minerals, and Equilibria*; Harper and Row: New York, NY, USA, 1965.
25. Rose, A.W. The effect of cuprous chloride complexes in the origin of red-bed copper and related deposits. *Econ. Geol.* **1976**, *71*, 1036–1048. [[CrossRef](#)]
26. Rose, A.W. Mobility of copper and other heavy metals in sedimentary environments. In *Sediment-Hosted Stratiform Copper Deposits*; Boyle, R.W., Brown, A.C., Jefferson, C.W., Jowett, E.C., Kirkham, R.V., Eds.; Geological Association of Canada Special Paper 36; Geological Association of Canada: Ottawa, ON, Canada, 1989; pp. 97–110.
27. Brown, A.C. A process-based approach to estimating the copper derived from redbeds in the sediment-hosted stratiform copper model. *Econ. Geol.* **2009**, *104*, 857–868. [[CrossRef](#)]
28. Hitzman, M.W.; Kirkham, R.V.; Broughton, D.; Thorson, J.; Selley, D. The sediment-hosted-stratiform copper ore system. In *Economic Geology 100th Anniversary Volume 1905–2005*; Hedenquist, J.W., Thompson, J.F.H., Goldfarb, R.J., Richards, J.P., Eds.; Society of Economic Geologists, Inc.: Littleton, CO, USA, 2005; pp. 609–642.
29. Vaughan, D.J.; Sweeney, M.; Diedel, F.R.; Haranczyk, C. The Kupferschiefer: An overview with an appraisal of the different types of mineralization. *Econ. Geol.* **1998**, *84*, 1003–1027. [[CrossRef](#)]
30. Sweeney, M.A.; Binda, P.L.; Vaughan, D.J. Genesis of the ores of the Zambian Copperbelt. *Ore Geol. Rev.* **1991**, *6*, 51–76. [[CrossRef](#)]
31. Selley, D.; Broughton, D.; Scott, R.; Hitzman, M.; Bull, S.; Large, R.; McGoldrick, P.; Croaker, M.; Pollington, N.; Barra, F. A new look at the geology of the Zambian Copperbelt. In *Economic Geology 100th Anniversary 1905–2005*; Hedenquist, J.W., Thompson, J.F.H., Goldfarb, R.J., Richards, J.P., Eds.; Society of Economic Geologists, Inc.: Littleton, CO, USA, 2005; pp. 965–1000.
32. Walker, T.R. Formation of red beds in modern and ancient deserts. *Geol. Soc. Am. Bull.* **1967**, *78*, 353–368. [[CrossRef](#)]
33. Walker, T.R. Application of diagenetic alterations in redbeds to the origin of copper in stratiform copper deposits. In *Sediment-Hosted Stratiform Copper Deposits*; Boyle, R.W., Brown, A.C., Jefferson, C.W., Jowett, E.C., Kirkham, R.V., Eds.; Geological Association of Canada Special Paper 36; Geological Association of Canada: Ottawa, ON, Canada, 1989; pp. 85–96.
34. Zielinski, A.; Bloch, S.; Walker, T.R. The mobility and distribution of heavy metals during the formation of first cycle red beds. *Econ. Geol.* **1983**, *78*, 1574–1589. [[CrossRef](#)]
35. Hanor, J.S. The sedimentary genesis of hydrothermal fluids. In *Geochemistry of Hydrothermal ore Deposits*, 2nd ed.; Barnes, H.L., Ed.; John Wiley and Sons: New York, NY, USA, 1979; pp. 137–172.
36. Henry, S.G.; Mauk, F.J.; van der Voo, R. Paleomagnetism of the Upper Keweenaw sediments: The Nonesuch Shale and Freda Sandstone. *Can. J. Earth Sci.* **1977**, *14*, 1128–1138. [[CrossRef](#)]
37. White, D.E. Environments of generation of some base-metal ore deposits. *Econ. Geol.* **1968**, *63*, 301–335. [[CrossRef](#)]
38. Bornhorst, T.J.; Williams, W.C. The Mesoproterozoic Copperwood sedimentary rock-hosted stratiform copper deposit, Upper Peninsula, Michigan. *Econ. Geol.* **2013**, *108*, 1325–1346. [[CrossRef](#)]

39. Elmore, R.D. The Copper Harbor Conglomerate and Nonesuch Shale: Sedimentation in a Precambrian Intracontinental Rift, Upper Michigan. Ph.D. Thesis, University of Michigan, Ann Arbor, MI, USA, 1981.
40. Walker, T.R. Diagenetic origin of continental red beds. In *The Continental Permian in Central, West and South Europe*; Falke, H., Ed.; Dordrecht, Reidel Publ. Co.: Dordrecht, The Netherlands, 1976; pp. 240–282.
41. Brown, A.C. Latent thermal effects from Porcupine Volcanics calderas underlying the White Pine-Presque Isle stratiform copper mineralization, northern Michigan. *Econ. Geol.* **2014**, *109*, 2035–2050. [[CrossRef](#)]
42. Symons, D.T.A.; Kawasaki, K.; Walther, S.; Borg, G. Paleomagnetism of the Cu-Zn-Pb-bearing Kupferschiefer black shale (Upper Permian) at Sangerhausen, German. *Miner. Depos.* **2010**, *46*, 137–152. [[CrossRef](#)]
43. Sillitoe, R.H.; Perello, J.; Garcia, A. Sulfide-bearing veinlets throughout the stratiform mineralization of the Central African Copperbelt: Temporal and genetic implications. *Econ. Geol.* **2010**, *105*, 1361–1368. [[CrossRef](#)]
44. Milton, J.E. Sedimentary Rock-Hosted Copper Mineralization in the Neoproterozoic Redstone Copperbelt, Northwest Territories, Canada. Ph.D. Thesis, University of British Columbia, Vancouver, BC, Canada, 2015; p. 396.



© 2017 by the author. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).